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TRITERPENES FROM THE LEAVES OF *PLEUROSTYLIA OPPOSITA*

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Key Word Index—*Pleurostylia opposita*; Celastraceae; triterpenes; lupanes.

Abstract—Friedelin, friedelan-3β-ol, sitosterol, α-amyrin, 6β,20-dihydroxylupan-3-one, lup-20(29)-en-3β,6β-diol, 6β,28-dihydroxylup-20(29)-en-3-one and dulcitol were isolated from the leaves of *Pleurostylia opposita*. The distribution of lupanes in the Celastraceae and their chemotaxonomic significance is discussed.

INTRODUCTION

Pleurostylia opposita is a moderately sized tree found in the dry zone of Sri Lanka. *Pleurostylia* was considered to be a monotypic genus but more recently *ca* six species [1] have been reported from Africa, Madagascar, Mascarenes, India, Sri Lanka, Indo-Malaysia, Queensland and New Caledonia. Two triterpenes, friedelin and epi-friedelinol, along with two alkaloids were isolated from the leaves of *P. africana* [2]. We have previously reported the isolation of pristimerin, sitosterol, α-amyrin and seven oxygenated lupanes from the stem bark of *P. opposita* [3, 4]. In this paper we report the triterpenes isolated from the leaves of *P. opposita* and include a survey of lupanes which have been found in the Celastraceae.

RESULTS AND DISCUSSION

Dried leaves of *Pleurostylia opposita* were extracted with benzene. The dark green solid obtained was separated by CC and prep. TLC. The compounds extracted from the benzene extract were friedelin, friedelan-3β-ol, sitosterol, α-amyrin, 6β,20-dihydroxylupan-3-one [3], lup-20(29)-en-3β,6β-diol [3] and 6β,28-dihydroxylup-20(29)-en-3-one [3]. It is noteworthy that friedelane derivatives were not isolated from the stem bark extract but 12% (dry wt) of the leaf extract consisted of friedelin and friedelan-3β-ol. Friedelane and lupane derivatives apparently do not co-exist in the stem bark. The only exception reported is in *Elaeodendron glaucum* [5] where subsequent work is at variance with this observation [6, 7]. The methanol extract of the leaves yielded mainly dulcitol which was characterized as its acetate. The quinone methide pristimerin, which was isolated from the stem bark extract to the extent of 14% [3] by weight of dry extract, was absent in the leaves.

The family Celastraceae consists of *ca* 850 species distributed among 55–60 genera [1, 8] which occur predominantly in the tropical and sub-tropical regions of both hemispheres [9]. Quinone methides such as pristimerin, the sugar alcohol, dulcitol, and the polyisoprene, gutta, are of widespread occurrence in the Celastraceae. The distribution of triterpenes in the Celastraceae has been reviewed [10]. The occurrence of friedelane derivatives from several species of a number of genera has been reported frequently [10–12] while lupanes have thus far been isolated from only seven genera of the Celastraceae (see Table 1).

Bentham and Hooker delineated the Celastraceae into the two tribes Celastreae and Hippocrateae, while the former was further divided into three sub-tribes [13]. Friedelane and lupane derivatives have been isolated from genera distributed among both tribes and also in genera from all three sub-tribes. Hence it is likely that lupanes are more widespread in the Celastraceae than hitherto believed.

EXPERIMENTAL

Mps were determined on a Kofler hot stage apparatus and are uncorr. Identities of compounds were established by mmp, co-TLC, IR and NMR comparison. Petrol refers to the fraction having boiling range 60–80° and prep. TLC was carried out on Merck Kieselgel 60 $PF_{254+365}$. Optical rotations were measured at 25° in $CHCl_3$. IR spectra were recorded using KBr discs. ^1H NMR spectra were recorded at 60 MHz with TMS as int. standard.

Extraction and isolation of compounds. (a) The dried and powdered leaves (1.1 kg) of *P. opposita* were extracted with C_6H_6 and then with MeOH. Evaporation of the C_6H_6 extract yielded a dark green solid (69.0 g) which was chromatographed on Si gel (petrol–EtOAc–MeOH).

Elution of the column with petrol and 5% EtOAc yielded friedelin (2.3 g), mp 257–258° (lit. [27], mp 257–265°); petrol and 20% EtOAc gave friedelan-3β-ol (2.5 g), mp 280–283° (lit. [27], mp 279–285°), then α-amyrin (0.75 g), mp 183–185° (lit. [28], mp 186°) and sitosterol (0.10 g), mp 134–135° (lit. [28], mp (136–137°); petrol and 25% EtOAc afforded 6β,20-dihydroxylupan-3-one (0.1 g), mp 249–250°, $[\alpha]_D - 37.8°$ (lit. [3], mp 249–252°, $[\alpha]_D - 37.5°$); petrol and 45% EtOAc gave lup-20(29)-en-3β,6β-diol (0.04 g), mp 196–198°. $(\alpha)_D + 4.0°$ (lit. [3], mp 196–198°, $[\alpha]_D + 4.0°$) and 6β,28-dihydroxylup-20(29)-en-3-one (0.20 g), mp 228–229°, $[\alpha]_D - 21.3°$ (lit. [3], mp 228–229°, $[\alpha]_D - 21.3°$).

(b) The MeOH extract (3g) was taken to dryness and acetylated at 65° with Ac_2O–pyridine. The product was crystallized from MeOH as colourless cubes of dulcitol acetate (0.70 g) mp 159–162° (lit. [6], mp 162–164°).

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Table 1.

Lupane derivative	Plant species	Reference
Lup-20(29)-en-3β-ol (lupeol)	*Celastrus scandens*	[14,15]
	Lophopetalum javanicum	[16]
	L. toxicum	[16]
	L. wightianum	[17,18]
	Salacia reticulata	[Wijeratne, D. B. T. and Kumar, V., unpublished]
Lup-20(29)-en-3β,28-diol (betulin)	*Maytenus senegalensis*	[18]
	Elaeodendron glaucum	[19]
	Lophopetalum javanicum	[16]
	L. toxicum	[16]
	L. wightianum	[18]
	Gymnosporia montana	[20]
Lup-20(29)-en-3-one(lupenone)	*Gymnosporia emarginata*	[21]
	Maytenus senegalensis	[22]
Lup-20(29)-en-23,28-diol	*Elaeodendron glaucum*	[5]
3-Oxo-lup-20(29)-en-28-oic acid (betulinic acid)	*E. glaucum*	[5]
3β-Hydroxy-(20*R*)-lupan-29-oic acid	*Gymnosporia wallichiana*	[23]
3β-Hydroxy-(20*S*)-lupan-29-oic acid	*G. wallichiana*	[23]
Lup-20(30)-en-3β,29-diol	*G. wallichiana*	[24]
3-Oxo-lup-20(29)-en-30-al	*Gymnosporia emarginata*	[25]
30-Hydroxylup-20(29)-en-3-one	*G. emarginata*	[25]
3β-Hydroxylup-20(29)-en-30-al	*G. emarginata*	[25]
20-Hydroxylupan-3-one	*Pleurostylia opposita*	[3]
Lupan-3β, 20-diol	*P. opposita*	[3]
6β,20-Dihydroxylupan-3-one	*P. opposita*	[3]
Lupa-5,20(29)-diene-3-one	*P. opposita*	[3]
Lup-20(29)-en-3β,6β-diol	*P. opposita*	[3]
6β,28-Dihydroxylup-20(29)-en-3-one	*P. opposita*	[3]
6β-Hydroxylup-20(29)-en-3-one	*P. opposita*	[4]
11α-Hydroxylup-20(29)-en-3-one	*Maytenus rigida*	[26]

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